

^{13}C and ^{18}O Labelling Fourier Transform I.R. Studies on C- and O-ended CO Chemisorption on Mn-promoted Rh/SiO₂ Catalysts

Masaru Ichikawa,^{a*} Pedro E. Hoffmann,^b and Atsushi Fukuoka^a

^a Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

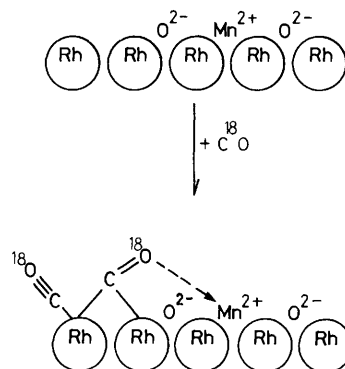
^b Departamento de Fisica, Facultad de Ciencias, Universidad de Los Andes 5105, Merida, Venezuela

I.r. spectroscopic evidence demonstrates the low frequency band of both C- and O-ended CO which interacts with Rh and a promoter Mn ion on a Rh-Mn/SiO₂ catalyst in the chemisorption and exchange of CO using ^{13}C O and C^{18}O .

It has been reported previously that additive metal ions such as Mn, Ti, and Zr provide a great enhancement of the CO conversion rates on Rh/SiO₂ catalysts in a CO hydrogenation reaction to give high yields of C₂-oxygenates such as ethanol and acetic acid.¹ In fact, the bifunctional promotion of the additive metals is a subject of recent interest and debate.² Ichikawa *et al.* found an activated CO band on the promoted Rh, characterised by the low frequency i.r. bands observed on CO chemisorption on Rh-Mn and Rh-Ti/SiO₂ catalysts.³ It has been proposed that the low frequency band arises from the CO chemisorbed in a tilted manner, *i.e.*, the carbon is bonded to two Rh atoms with the oxygen interacting with the promoter cations.⁴ In this Communication, we report further Fourier transform (F.t.) i.r. spectroscopic evidence for the C- and O-ended CO on Rh-Mn/SiO₂ by using ^{13}C O and C^{18}O .

The catalyst Rh-Mn/SiO₂ (Rh:Mn = 1:2 atomic ratio, 4 wt% Rh loading) was prepared by co-impregnation of SiO₂ (Aerosil 300) with a methanol solution of RhCl₃·3H₂O and MnCl₂·4H₂O. After removal of the solvent under vacuum, followed by reduction in flowing H₂ (1 atom, 100 ml/min) with programmed heating from 25 to 400 °C for 6 h, the resultant Rh-Mn/SiO₂ was pressed into a thin disk (20 mm φ, 25 mg) for mounting in the *in situ* i.r. cell. I.r. spectra were recorded on an F.t. double-beam i.r. spectrometer (Shimadzu FTIR-4100) with a resolution of 2 cm⁻¹. ^{13}C O (98% enriched) and C^{18}O (90% enriched) were purchased from MSD Isotope Co. and dried with Molecular Sieve 5A.

Upon admission of CO (150 mmHg) at 25 °C onto the freshly reduced Rh-Mn/SiO₂, a characteristic low frequency CO band (LF CO) appeared at 1713 cm⁻¹ as well as the usual bands of linear (at 2055 cm⁻¹) and bridging CO (at 1815 cm⁻¹), as shown in Figure 1. The relative rates of growth for each band on CO chemisorption at 25 °C on Rh-Mn/SiO₂ were in the following order: LF CO \gg bridging CO > linear CO. This suggests that the CO species giving the LF CO band is more activated by the Rh-Mn sites compared with the bridging and linear CO species.



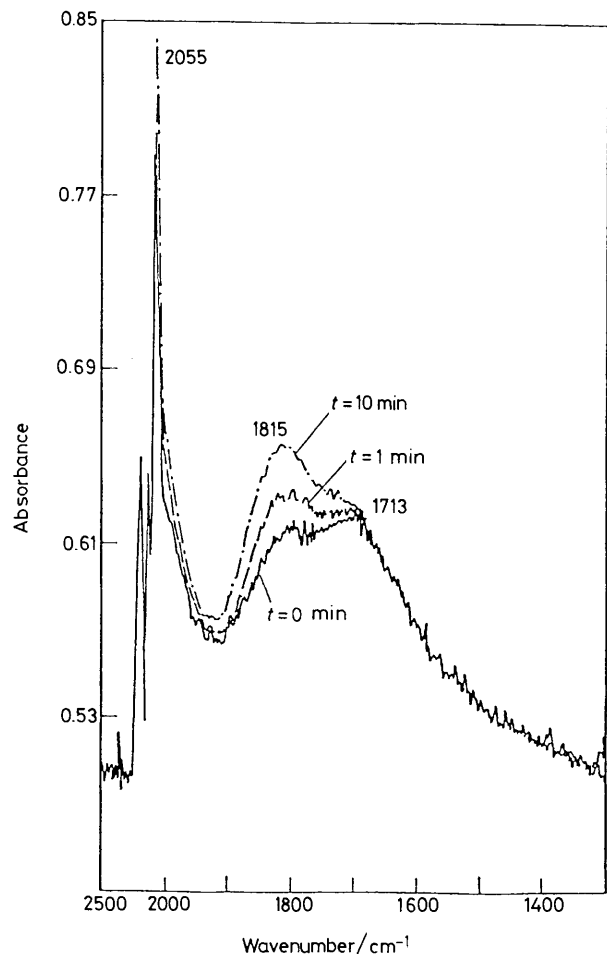


Figure 1. I.r. spectra of CO chemisorption on Rh-Mn/SiO₂ (Rh : Mn = 1 : 2) at 25 °C. CO = 150 mmHg; *t* = 0, 1, and 10 min after admission of CO on the H₂-reduced catalyst.

In the F.t.i.r. spectrum after the chemisorption of ¹³CO (50 mmHg) at 25 °C on the H₂-reduced Rh-Mn/SiO₂ catalyst [Figure 2(a)], the bands at 2012 and 1770 cm⁻¹ are assigned to linear and bridging ¹³CO, respectively, with a shift of ca. 40 cm⁻¹ from the bands on CO chemisorption due to the isotope effect. The LF ¹³CO band was observed at 1670 cm⁻¹ overlapping with the broad band of bridging ¹³CO. It is notable that among the chemisorbed ¹³CO, the linear and bridging ¹³CO exchanged rapidly with gaseous ¹²CO at 25 °C, while the LF ¹³CO gave a very low rate of the exchange even at 50 °C. This indicates that the LF CO species has a stronger bonding with the Rh-Mn sites than the linear and the bridging CO species do. On chemisorption of C¹⁸O (25 mmHg) at 25 °C [Figure 2(b)], we observed the bands at 2010 and 1797 cm⁻¹ attributable to linear and bridging C¹⁸O, respectively. Additionally, the broad band in the region of 1850–1650 cm⁻¹ consists of two overlapping bands; a shoulder band is observed at ca. 1700 cm⁻¹, which is similar to the position of LF C¹⁶O, rather than the expected value of ca. 1660 cm⁻¹ for C¹⁸O. This suggests that facile ¹⁸O to ¹⁶O exchange had occurred involving ¹⁸O in the catalyst. When C¹⁶O (150 mmHg) was admitted onto the C¹⁸O chemisorbed Rh-Mn/SiO₂ at 25 °C [Figure 2(c)], the broad band was resolved into two bands. One band corresponds to the bridging C¹⁶O at 1815 cm⁻¹ and the other to the LF C¹⁶O at 1713 cm⁻¹, which is in good agreement with the bridging C¹⁶O and the LF C¹⁶O band

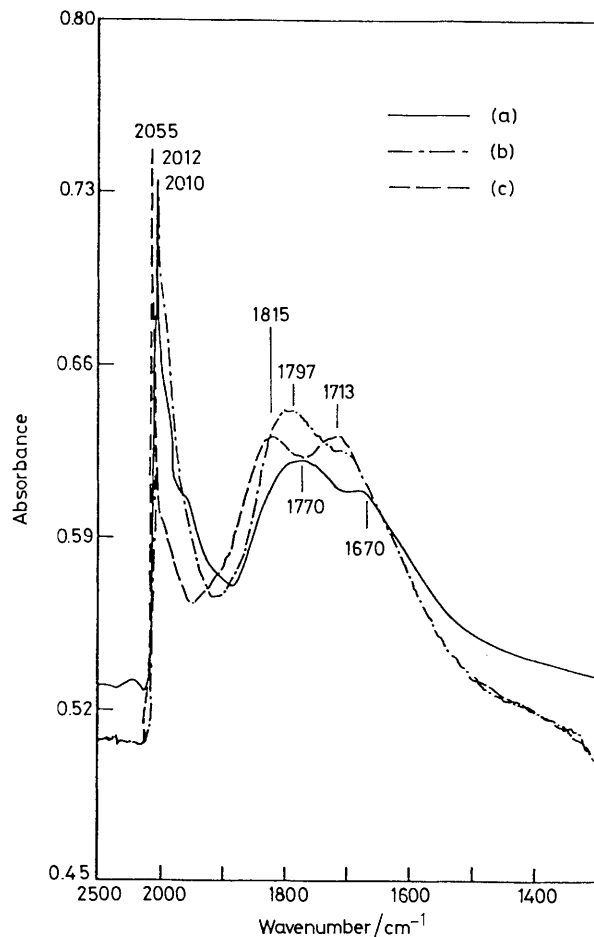


Figure 2. I.r. spectrum of ¹³CO and C¹⁸O chemisorption on Rh-Mn/SiO₂ (Rh : Mn = 1 : 2) at 25 °C. (a) ¹³CO chemisorption, ¹³CO = 50 mmHg; (b) C¹⁸O chemisorption, C¹⁸O = 25 mmHg; (c) admission of CO (150 mmHg) on the C¹⁸O chemisorbed Rh-Mn/SiO₂ at 25 °C.

observed in the C¹⁶O chemisorption on Rh-Mn/SiO₂ in Figure 1. Accordingly, it is proposed that the LF CO species is active for the facile exchange of oxygen possibly with promoter MnO on Rh-Mn/SiO₂ as in Scheme 1. The formation of the C- and O-ended CO on Rh-Mn/SiO₂ is suggested to promote the CO dissociation, resulting in the increase of CO conversion rates and high yields of C₂-oxygenates in the CO hydrogenation reaction.

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